

# Preparation of Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrodes for anodic oxidation of pharmaceutical drugs

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**Abstract** Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrodes were prepared by alternating Sn and Sb electrodepositions, repeated 4 or 16 times, onto a platinized titanium foil by a thermo-electrochemical method. Chemical, electrochemical, and structural tests have been used for the characterization of Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrodes. Anodic oxidation of the aqueous solution contaminated by amoxicillin, clofibric acid, diclofenac, and ibuprofen having a concentration of 100 mg L<sup>−1</sup> and 0.035 M of Na<sub>2</sub>SO<sub>4</sub> have been applied using Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrodes at a current density of 10 and 30 mA cm<sup>−2</sup>. The chemical oxygen demand removals increased with current density and except for diclofenac, the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrode with 4 electrodeposition repetitions gave the best results. The combustion efficiencies for diclofenac and ibuprofen were higher than those obtained with similar electrode material, prepared without platinization, especially in the assay run with Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> (16 electrodeposition repetitions).

**Keywords** Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> anode · Anodic oxidation · Amoxicillin · Clofibric acid · Diclofenac · Ibuprofen

## 1 Introduction

Drugs are reaching the aquatic environment and, despite their very low concentrations, up to μg L<sup>−1</sup>, presenting a

potential hazard for human health, such as the increase of antibiotic-resistant bacterial infections, especially in locations where advanced wastewater treatments are not used [1–3]. In fact, there are studies concerning the presence of pharmaceutical compounds in the effluents of municipal sewage treatment plants [4–6].

Electrochemical oxidation treatment is a potential alternative method for eliminating pollutants with good efficiency. However, for the elimination of organic pollutants, it requires an anode with a high oxygen overpotential, high electrical conductivity, and suitable mechanical and electrochemical stability.

Several electrode materials, such as boron-doped diamond (BDD), PbO<sub>2</sub>, and doped SnO<sub>2</sub>, have performed well in the electrodegradation of pharmaceutical compounds [7–17]. However, their disadvantages include the high cost for BDD anodes, the possibility of lead contamination for PbO<sub>2</sub>, and the short service life for Ti/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> anodes.

The metal/substrate interaction can influence the chemisorption and the catalytic properties of the supported metal oxides. A few authors have studied the performance of Ti/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrodes and concluded that these electrodes, when working as anodes, have a short service life due to the formation of a TiO<sub>2</sub> interlayer with a higher resistivity than Ti. This layer can be formed during the electrode preparation or during its use as an anode because the oxide films have appreciable porosity. In both cases, TiO<sub>2</sub> interlayer formation is inevitable.

The formation of an undesirable TiO<sub>2</sub> interlayer has been the subject of many studies: the addition of Pt to the SnO<sub>2</sub> film [18–21], prior platinization of the Ti substrate followed by SnO<sub>2</sub> deposition [22], addition of IrO<sub>2</sub>, or an isomorphous structure interlayer [23–26] or a RuO<sub>x</sub> [26] or Sb<sub>2</sub>O<sub>4</sub> interlayer [27, 28] between the Ti and SnO<sub>2</sub>. All procedures increased the service life of the electrodes, in

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some cases by up to two orders of magnitude [23]. Recently, chemical vapor deposition (CVD), without  $O_2$  as a precursor, was used in the preparation of Ti/SnO<sub>2</sub> anodes, avoiding the formation of the TiO<sub>2</sub> passivation layer [29]. These electrodes presented a compact microstructure with a high overpotential for oxygen evolution and a superior activity for pollutant oxidation.

Chen and co-workers [30] have presented values for the service life of SnO<sub>2</sub> electrodes with iridium oxide, antimony oxide, or ruthenium oxide under different experimental conditions, achieving service lives from 500 to 1,600 h.

Montilla and co-workers [19] have studied the effect of introducing small quantities of platinum in Ti/SnO<sub>2</sub>-Sb electrodes. The electrodes with higher Pt contents have presented higher capacitance and a higher roughness factor, up to 1,190, an increase of one order of magnitude.

Our research group has also prepared Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> anodes [14] for the degradation of pharmaceutical compounds with good results. However, the service life of those electrodes was approximately one week at current densities ranging from 10 to 30 mA cm<sup>-2</sup>. This short service life was most likely due to the formation of a non-conductive titanium interlayer that disables the electrode. To this end, the objective of the present work is to improve the electrodes' service life by introducing a platinum interlayer between the titanium substrate and metal oxides, yielding Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> electrodes. The platinum interlayer is expected to prevent the formation of titanium oxide.

## 2 Materials and methods

### 2.1 Chemicals

The following reagents were used as purchased in the preparation of the electrodes: titanium foil (99.7 %, Sigma-Aldrich); sodium hydroxide (96.8 %, Pronalab); oxalic acid (99 %, Merck); chloridric acid (37 %, Pronalab); H<sub>2</sub>PtCl<sub>6</sub>·xH<sub>2</sub>O (99.9 %, Sigma-Aldrich); tin(II) chloride (98 %, Sigma-Aldrich); antimony(III) chloride (99 %, Fluka); and citric acid (100 %, Pronalab). The chemicals used as model pollutants and electrolyte were amoxicillin (AM) (90 %, Aldrich); clofibric acid (CA) (97 %, Sigma-Aldrich); sodium diclofenac salt (DIC) (99 %, Sigma-Aldrich); sodium ibuprofen salt (IBU) (99.8 %, Sigma-Aldrich); and sodium sulfate (99 %, Merck).

### 2.2 Preparation of Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> anodes

Ti substrates, with dimensions of 2 cm × 2.5 cm × 0.25 mm, were pre-treated by mechanical polishing followed by etching with 40 % NaOH (w/w) at 80 °C for 2 h

and 15 % oxalic acid (w/w) at 98 °C for 1 h. The substrates were then washed with double-distilled water. Substrate platinization was performed in a one-compartment double-walled cell connected to a thermostatic water bath, which enabled the recirculation of water at 65 °C. The cell contained a chloroplatinic acid solution, and a current density of 250 mA cm<sup>-2</sup> was applied [31] using the Ti substrate as the cathode and two platinum plates as anodes. After platinization, alternate Sn and Sb electrodepositions on the Ti substrate were carried out in the same cell. For the Sn deposition, 100 mL of an aqueous solution with 0.948 g of SnCl<sub>2</sub> and 2 mL of concentrated chloridric acid was used with a current density of 10 mA cm<sup>-2</sup> maintained for 30 min at 35 °C. For the Sb deposition, 100 mL of an aqueous solution with 1.329 g of SbCl<sub>3</sub> and 3.842 g of citric acid was used with a current density of 10 mA cm<sup>-2</sup> maintained for 10 min at 35 °C. These two procedures were repeated 4 or 16 times to prepare two different electrodes: Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) and Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16).

After this treatment, the electrodes were heated in a tubular furnace at 550 °C for 6 h to obtain the respective oxides. The geometric area of the prepared electrodes was 10 cm<sup>2</sup> (both sides). The oxide loading was approximately 15 mg cm<sup>-2</sup> for Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) and 50 mg cm<sup>-2</sup> for Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16).

The electrodes were structurally characterized by X-ray powder diffraction (XRD) at room temperature using a Rigaku DMAXIII/C diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm) at 30 kV/40 mA. The diffraction patterns were collected in the range of  $2\theta$  = 10–90° with a 0.02° step and an acquisition time of 2 s per step. The morphologies were then evaluated by scanning electron microscopy (SEM), and microanalysis was performed by dispersive energy spectroscopy (EDS) in a Hitachi (S-2700)/Oxford (60–74) system operating at 20 keV.

### 2.3 Electrochemical studies

#### 2.3.1 Voltammetric studies

The cyclic voltammetric measurements were performed using a potentiostat/galvanostat VoltaLab PGZ 301, in a one-compartment cell, with a 10 cm<sup>2</sup> Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) or (16) electrode as the working electrode, a 5 cm<sup>2</sup> (per side) platinum plate as the counter electrode and a commercial saturated Ag/AgCl, and KCl<sub>sat</sub> electrode as the reference electrode. Voltammograms were recorded at scan rates between 2 and 50 mV s<sup>-1</sup> in 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution without and with pollutant concentrations of 1 g L<sup>-1</sup> with the exception for clofibric acid, the solubility of which is lower and for which a saturated solution was used.

### 2.3.2 Electrodegradation assays

Electrodegradation experiments were conducted in a 250 mL undivided cell in batch mode with stirring. The anode and cathode were a Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(*n*) electrode and a stainless steel foil, respectively, both of which were 10 cm<sup>2</sup> in area with a 2 cm gap between them. All anodic oxidation assays were performed under galvanostatic conditions with imposed current densities of 10 or 30 mA cm<sup>−2</sup>. The processed solution volume was 200 mL with a concentration of 100 mg L<sup>−1</sup> of AM (COD<sub>0</sub> = 137 ± 1 mg L<sup>−1</sup>; TOC<sub>0</sub> = 45 ± 2 mg L<sup>−1</sup>), CA (COD<sub>0</sub> = 160 ± 3 mg L<sup>−1</sup>; TOC<sub>0</sub> = 54 ± 1 mg L<sup>−1</sup>), DIC (COD<sub>0</sub> = 138 ± 3 mg L<sup>−1</sup>; TOC<sub>0</sub> = 49 ± 2 mg L<sup>−1</sup>), or IBU (COD<sub>0</sub> = 200 ± 9 mg L<sup>−1</sup>; TOC<sub>0</sub> = 64 ± 2 mg L<sup>−1</sup>). Sodium sulfate aqueous solutions (0.035 M) were used as the supporting electrolyte in all experiments. Assays were run for 24 h, and data points were collected at 2 h intervals for first 8 h with a final data point collected at 24 h. The degradation of the organic pollutants was followed by UV–visible absorption spectrophotometry with the absorbance measurements between 200 and 800 nm using a UNICAM He $\lambda$ ios- $\alpha$  UV/VIS spectrophotometer. The chemical oxygen demand (COD) was determined by the titrimetric method with closed reflux [32]. The decrease in the organic carbon content during the assays was monitored by the measurements of the total organic carbon (TOC) performed in a Shimadzu TOC-V<sub>CPH</sub>/CPN apparatus. All the assays were repeated twice, and the COD and TOC values presented are mean values.

## 3 Results and discussions

### 3.1 Electrode characterization

#### 3.1.1 Structural characterization by DRX

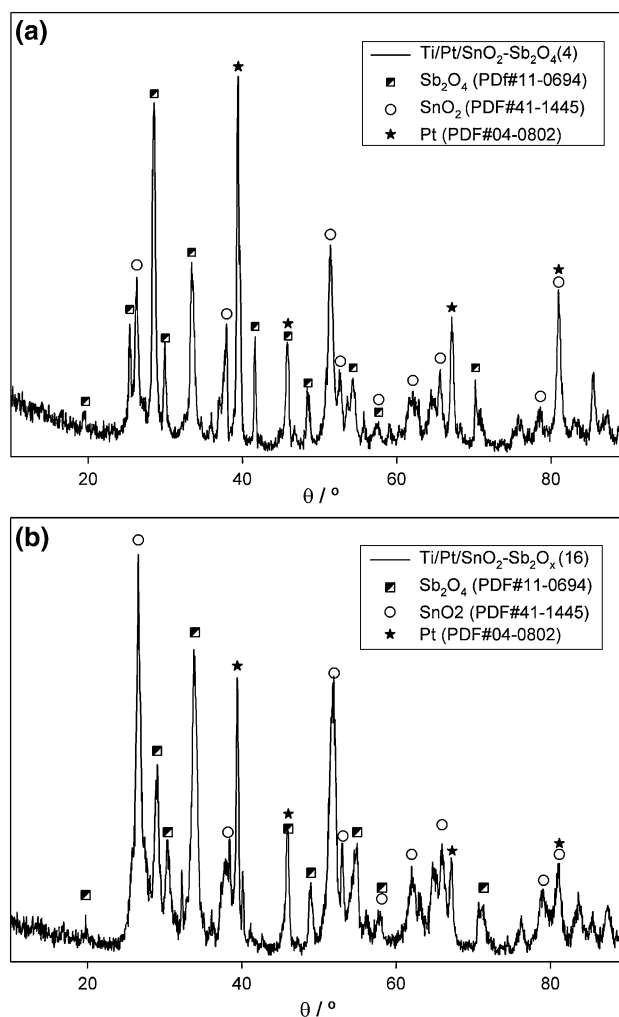
After calcination at 550 °C, an X-ray diffractogram of the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(4) electrode was obtained (Fig. 1a) and compared with those from the JCPDS ICDS database. The presence of the Sb<sub>2</sub>O<sub>4</sub> (file PDF#11-0694, relative to an orthorhombic structure with *a* = 5.436 Å, *b* = 4.81 Å and *c* = 11.76 Å) and SnO<sub>2</sub> (file PDF # 41-1445, tetragonal structure with *a* = *b* = 4.7382 Å and *c* = 3.1871 Å) phases were confirmed. A platinum phase was also identified (PDF # 04-0802). A diffractogram of the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(16) electrodes obtained after final calcination at 550 °C is presented in Fig. 1b, and the identical phases for SnO<sub>2</sub>, Sb<sub>2</sub>O<sub>4</sub>, and platinum were also identified. However, comparing both diffractograms, the crystallites' orientation must be different because the relative intensity of the same diffraction lines differs between the two diffractograms.

#### 3.1.2 Morphological characterization by SEM

Morphology view of the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(4) and (16) electrodes, before and after use for pollutant degradation, are presented in Fig. 2. Before use, the morphology of the platinized electrodes is quite different from that of the Ti/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> electrodes prepared in a similar way, but without platinization, which presented the characteristics of cracked mud [14, 22, 25]. In fact, the morphology views of Fig. 2 show a granular morphology, indicating that the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub> film is a more compact coating. The film appearances were almost identical before and after use.

#### 3.1.3 Chemical characterization by EDS

The results from the EDS analysis of the final stage of the metal oxide electrodes, in atomic molar percentages, were



**Fig. 1** X-ray diffractogram of the **a** Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(4) and **b** Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(16) composite oxide electrodes in their final form after calcination at 550 °C

as follows: Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4), O-74 %, Sn-9 %, and Sb-17 % and Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16), O-80 %, Sn-6 %, and Sb-14 %. In both materials, the Sb content was higher than expected, possibly because the final layer consists of antimony, which is more easily detected by EDS.

### 3.1.4 Electrochemical characterization by cyclic voltammetry

The relative roughness factor [33],  $R_f$ , of the electrode coating was estimated by running cyclic voltammetric curves with the Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> electrodes as the working electrode in a one-compartment electrochemical cell. Because the electrode was made of conductive oxides, the double-layer charging current,  $I$ , which is closely related to the double-layer capacitance,  $C$ , of the electrode/solution interface, is linearly dependent on the scanning rate,  $v$ . Figure 3 presents several cyclic voltammograms recorded at different scan rates between 2 and 50 mV s<sup>-1</sup> in 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution from 0.6 to 0.8 V versus Ag/AgCl, KCl<sub>sat</sub>. As observed, only double-layer charging currents were observed. From the above-mentioned current–potential curves, the  $I$  values for the different scan rates

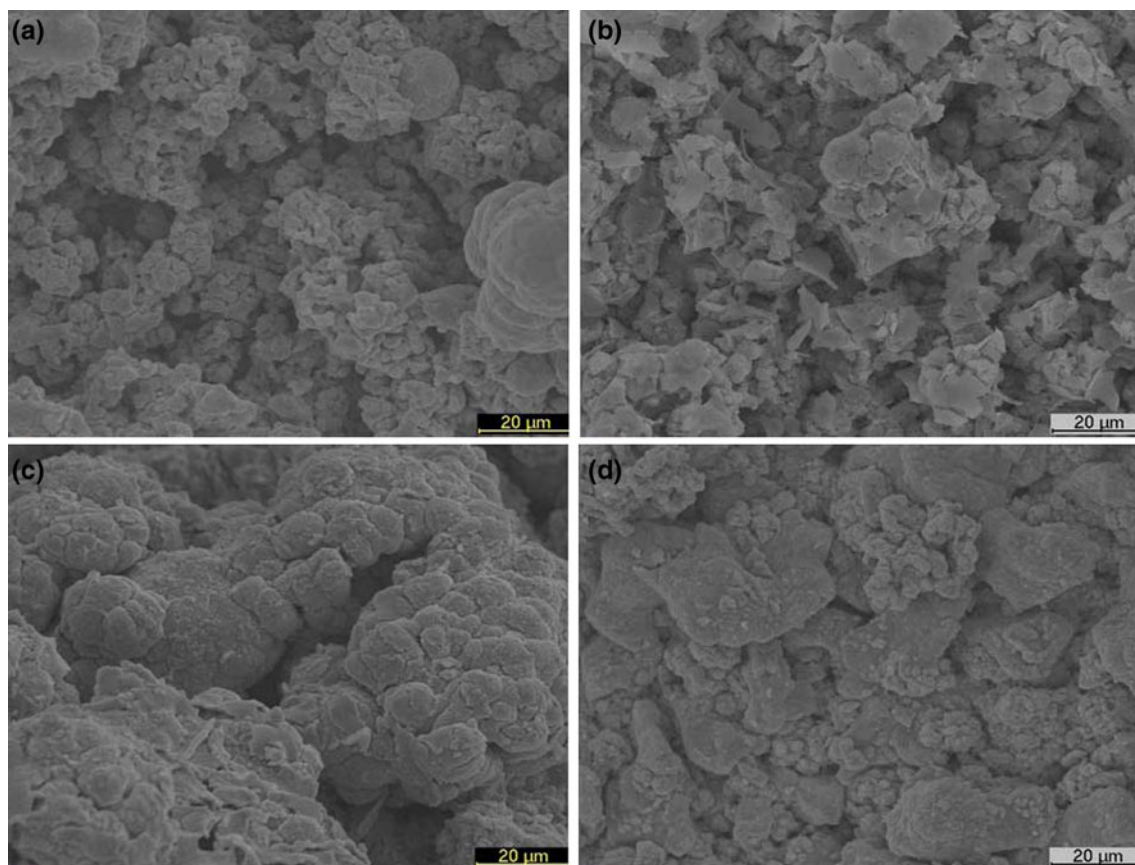
were obtained at  $E = 0.7$  V versus Ag/AgCl, KCl<sub>sat</sub>, the point at which an approximate symmetry for the anodic and cathodic currents was observed. From the plot of  $I$  versus  $v$  for the Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) electrode (Fig. 3a and inset), the following linear equation was obtained:

$$I(A) = 0.0245v(V s^{-1}) + 0.000068, \text{ with } r^2 = 0.997 \quad (1)$$

Dividing the slope value by the geometric area of the electrode yields the normalized capacitance of the oxide/solution interface ( $C = dq/dE = dI/dv$ ),  $C_{\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4} = 0.00245 \text{ F cm}^{-2}$ . To estimate the relative roughness factor of the Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) film, its capacitance was compared with that of an oxide with a smooth surface, which was assumed to be 60 μF cm<sup>-2</sup> [33], providing a  $R_f$  of 41 for the prepared material. A similar study was performed for Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16) (see Fig. 3b and inset), and the following equation was obtained:

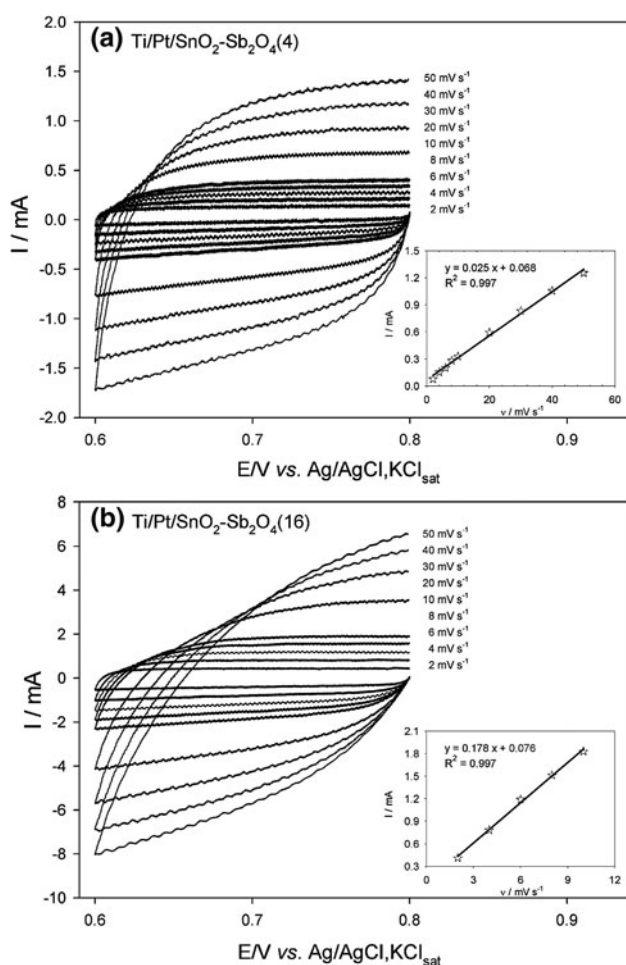
$$I(A) = 0.178v(V s^{-1}) + 0.000076, \text{ with } r^2 = 0.997 \quad (2)$$

The normalized capacitance obtained for this electrode was 0.0178 F cm<sup>-2</sup>, which corresponds to a roughness



**Fig. 2** Morphology views of Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4), **a** before and **b** after being used as electrode (530 h), and Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16), **c** before and **d** after being used as electrode (520 h). Magnification: ×1000





**Fig. 3** Cyclic voltammogram for Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(n) (10 cm<sup>2</sup>) obtained at the double-layer region for scan rates from 2 to 50 mV s<sup>−1</sup> in a 0.035 M Na<sub>2</sub>SO<sub>4</sub> solution: **a** n = 4; **b** n = 16. Insets: Linear regression of I versus v measured at E = 0.7 V

factor of 297. Thus, the increase in the number of metal layers increased the roughness of the electrode surface.

In a previous work with these electrodes [14], which were not platinized, with four alternate depositions of each metal, a normalized capacitance of 0.0466 F cm<sup>−2</sup> and a roughness factor of 777 were obtained for the double-layer capacitance; however, the deposition time for each metal was four times longer. The roughness factors were lower for the platinized electrodes prepared in this work, likely due to the lower metal deposition time used in this case, which prevents the growth of surface imperfections and decreases the roughness factor of the films. The metal deposition time was reduced to avoid excessive imperfections, which fall into the solution and increase electrode preparation costs.

Wu et al [34] have prepared amorphous tin oxide (SnO<sub>x</sub>) films by cathodic deposition on graphite, achieving a specific capacitance of 0.255 F cm<sup>−2</sup> and a roughness factor of 4167, which is much higher than that obtained in this

work. This order-of-magnitude discrepancy between roughness factors is not unusual; the literature includes roughness factors for metal oxide films that vary by factors of several thousand.

### 3.2 Electrochemical studies of the pharmaceutical compounds

#### 3.2.1 Voltammetric studies

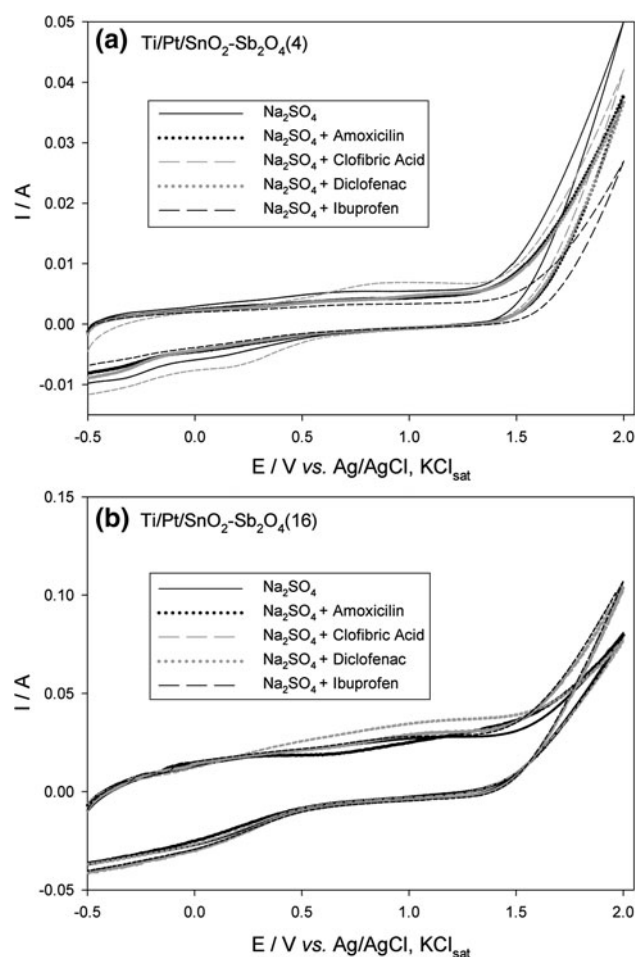
To avoid the reduction of Sn or Sb ions at the electrode surface, voltammograms were only run for potentials above −0.5 V. The voltammograms for Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(4)/Na<sub>2</sub>SO<sub>4</sub> (0.035 M) were run for different organic concentrations and scan rates, and the best defined peaks were obtained at a scan rate of 20 mV s<sup>−1</sup> (Fig. 4a). In the presence of the pollutant mixture, only clofibric acid presents an anodic peak (near 0.7 V), indicating that this compound could be degraded most easily and is the only one that can be oxidized before the oxygen evolution zone.

Figure 4b presents the cyclic voltammograms obtained with the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(16) layers in Na<sub>2</sub>SO<sub>4</sub> (0.035 M) + pollutant system at a scan rate of 20 mV s<sup>−1</sup>, which produced the best defined peaks. As observed for the previous electrode, only clofibric acid presents a distinct behavior.

Despite the observations for clofibric acid, to perform the complete oxidation of the studied pollutants and metabolites that may result from the first steps of the oxidation and to avoid the formation of passivating organic films on the electrode surface, which occurs for low applied potentials, the electrodegradation assays were run at higher current densities, 10 and 30 mA cm<sup>−2</sup> for all compounds. These current densities guaranteed an applied potential high enough to allow the complete oxidation of organics and to prevent passivation. In addition, the use of high current densities will test the electrochemical and mechanical stability of the prepared materials.

#### 3.2.2 Electrodegradation assays

Table 1 presents the COD, TOC, and Abs removals by the assays performed with both anode materials during the degradation of the four pharmaceutical compounds during 8 and 24 h. Figures 5, 6, and 7 display the relative decays in Abs, COD, and TOC, respectively, with time for the assays run with the four pharmaceutical compounds under the different experimental conditions. The absorbances were measured at the characteristic wavelength of each compound. Faster decays in absorbance were always obtained for the Ti/Pt/SnO<sub>2</sub>–Sb<sub>2</sub>O<sub>4</sub>(4) anode in the assays performed at 30 mA cm<sup>−2</sup>. For this anode, and except for the CA, for which the absorbance decay rate is almost



**Fig. 4** Cyclic voltammograms for  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(n)$  in 0.035 M  $\text{Na}_2\text{SO}_4$  with and without 1000 ppm pollutant (except clofibric acid, the solution of which was saturated). Scan rate:  $20 \text{ mV s}^{-1}$ . Electrode geometric area:  $10 \text{ cm}^2$ . **a**  $n = 4$ ; **b**  $n = 16$

independent of the current density, the absorbance removal rate increases with current density. For the  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(16)$  electrode, the influence of current density is less significant. In fact, after 8 h, the Abs removals are almost independent of current density for AM and CA and are higher for the highest current density in the case of DIC and IBU. As shown in the UV-vis spectra presented in the insets for the lower current density assayed with the  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(4)$  anode, AM and DIC exhibit a regular decay up to 8 h, after which the solution becomes turbid. In the case of CA, a new band appears near 256 nm, and for IBU, an increase in the band at 262 nm is observed. This behavior for IBU is typical and is usually associated with the formation of 2-[4-(carboxycarbonyl)phenyl]propanoic acid by the attack of the hydroxyl radicals to the IBU molecule [11].

Regarding the relative COD removals, the best results for AM and CA were obtained with  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(4)$  anode at the higher current density, which, for this anode,

has a positive influence on the removal rate. For the same assays performed with  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(16)$  anode, the current density had almost no influence on the COD removal rate. Only in the case of DIC did the  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(16)$  anode perform better in the COD abatement. For this anode, the applied current seems to have a marked influence on the mechanism, as observed by the form of the COD removal profile. In the assays performed with IBU at  $30 \text{ mA cm}^{-2}$ , the COD removal rates were similar for both anode materials. However, at  $10 \text{ mA cm}^{-2}$ , the COD removal was lower for the  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(16)$  anode. This material presents higher porosity than  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(4)$  and, at low current density, the slower formation of oxygen bubbles, from oxygen evolution, may hinder the electrode's surface. This problem is overcome at high current density, since the oxygen evolution is so high that bubbles coalesce and are released more easily, unblocking the electrode's surface.

Regarding the TOC variation in time for the assay performed with AM (Fig. 7a), the best results were obtained with  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(4)$  at the higher current density. At the lower current density, the results are very similar for both anode materials with the worst results achieved by  $\text{Ti/Pt/SnO}_2\text{-Sb}_2\text{O}_4(16)$  at higher current density, as had already been observed for COD. For CA and DIC, the best TOC removals were obtained at lower current densities for both anode materials tested. This different behavior is related to the existence of chlorine atoms in the molecules; its presence usually increases the COD removal rate and decreases the TOC removal rate, which should be more pronounced at a higher current density due to the low Cl content in the solution. For IBU, the results do not seem to depend strongly on the anode material and the TOC removal rate increases with current density.

The COD and TOC removals obtained in the degradation of IBU and DC with these  $\text{SnO}_2\text{-Sb}_2\text{O}_4$  platinized electrodes were slightly lower than those obtained with a nonplatinized  $\text{SnO}_2\text{-Sb}_2\text{O}_4$  electrode at  $10 \text{ mA cm}^{-2}$  recorded in a previous study [14]. This behavior is related to the presence of platinum, as shown in the X-ray diffractogram, which is known by its ability to adsorb pollutant molecules, thus changing the reaction mechanism. However, the pre-platinization of the titanium electrode substrate significantly improves the service life of these electrodes.

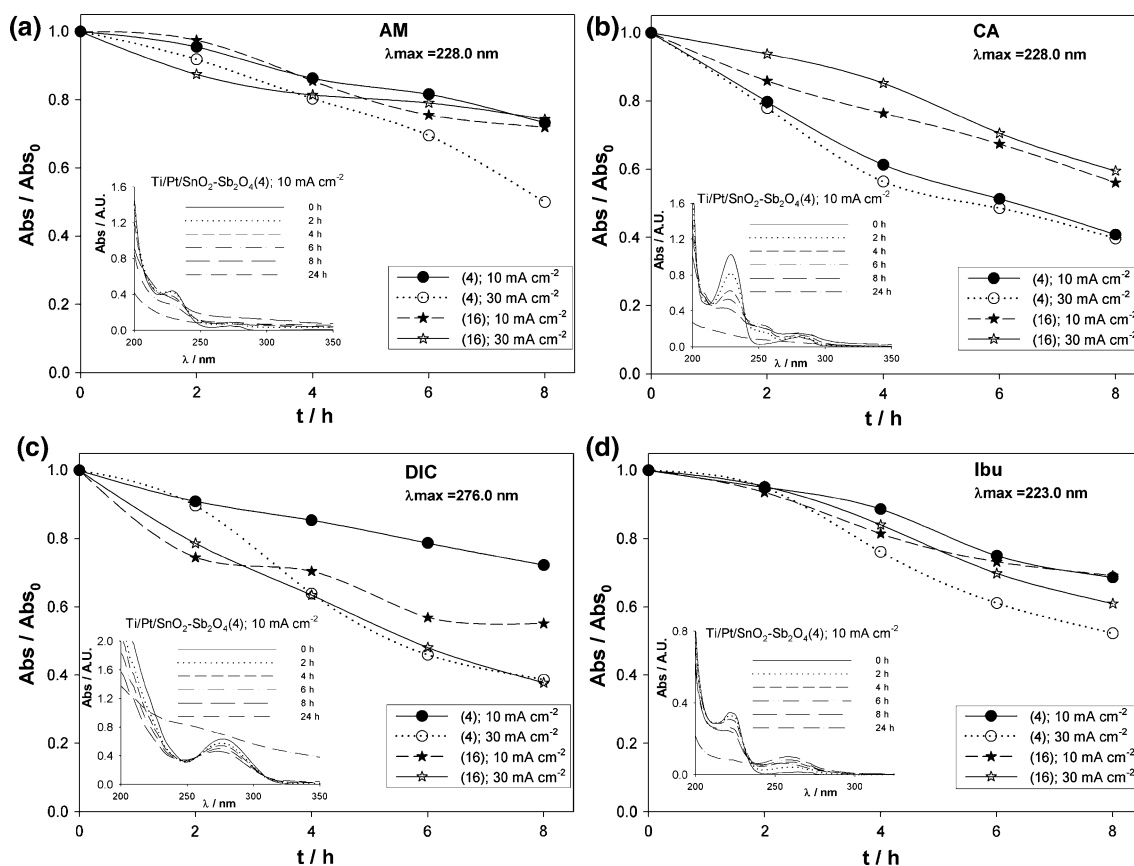
To compare the materials used in this work and the  $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_4$  electrode [14], the combustion efficiencies,  $\eta_c$ , were calculated for the pharmaceutical compounds using the three different electrode materials by eq. (3) [35]:

$$\eta_c = \frac{32}{12} \left( \frac{n}{4x} \right) \frac{d\text{TOC}}{d\text{COD}} \quad (3)$$

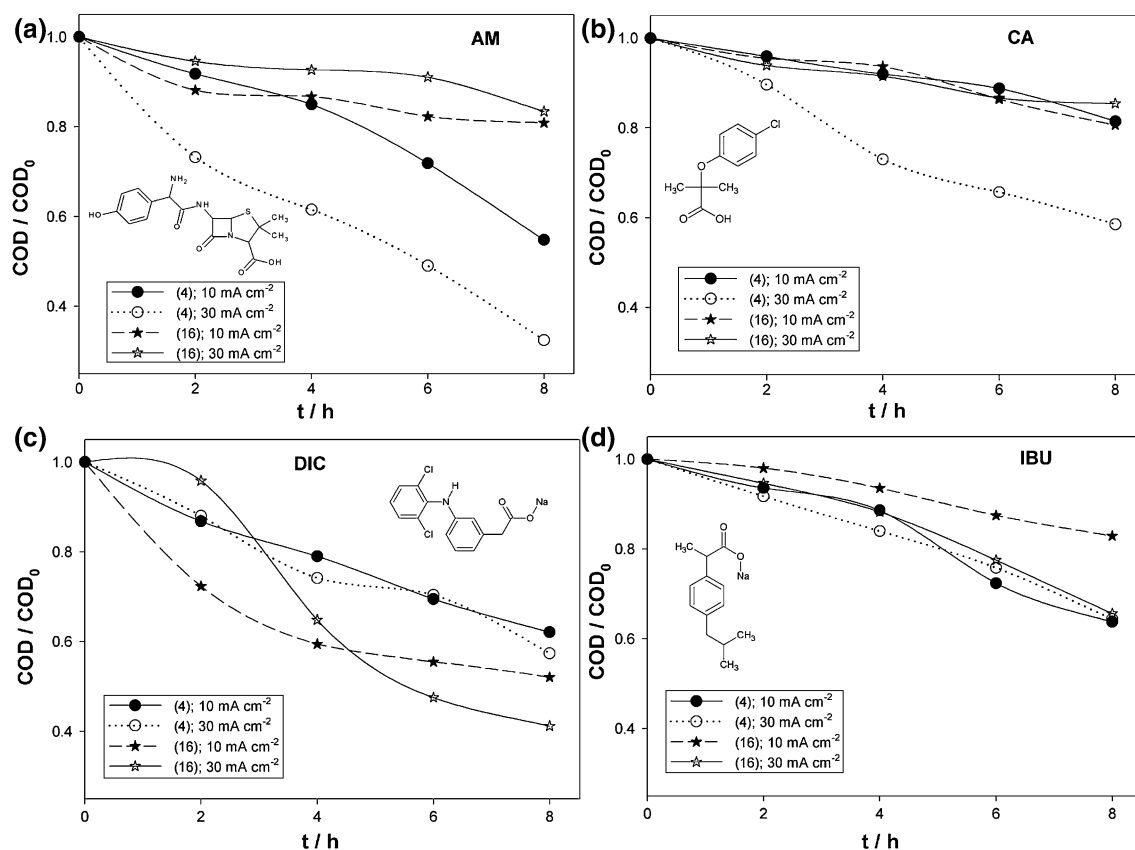
where TOC is in  $\text{mg}_C \text{ L}^{-1}$ , COD is in  $\text{mg}_{\text{O}_2} \text{ L}^{-1}$ ,  $n$  is the number of electrons transferred to the electrode in the

**Table 1** COD, TOC, and absorbance (Abs) % removals for the different electrode materials and compounds tested after 8 and 24 h assays

Electrode material		Ti/Pt/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> (4)				Ti/Pt/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> (16)			
Current density		10 mA cm <sup>-2</sup>		30 mA cm <sup>-2</sup>		10 mA cm <sup>-2</sup>		30 mA cm <sup>-2</sup>	
Assay time		8 h		24 h		8 h		24 h	
Pollutant	Parameter	% Removal							
Amoxicillin	COD	45	64	68	79	19	46	17	44
	TOC	27	51	35	49	27	38	33	41
	Abs	27	72	50	70	28	53	26	72
Clofibric acid	COD	19	46	42	64	19	41	15	37
	TOC	32	50	28	55	15	58	11	65
	Abs	59	86	50	93	44	76	41	74
Diclofenac	COD	38	52	43	71	48	57	59	71
	TOC	47	— <sup>a</sup>	38	60	49	67	41	64
	Abs	28	— <sup>a</sup>	61	93	45	63	62	88
Ibuprofen	COD	36	75	36	75	17	46	34	82
	TOC	24	61	40	78	22	57	34	75
	Abs	31	76	48	77	31	70	39	91

<sup>a</sup> Not determined due to the solution's high turbidity**Fig. 5** Relative absorbance (Abs) decay for the assays run with the different pollutants (**a** AM; **b** CA; **c** DIC; **d** IBU) measured at the characteristic wavelength of each compound and run at two different current densities, 10 and 30 mA cm<sup>-2</sup>. Experimental conditions:

100 mg L<sup>-1</sup> pollutant in 200 mL of 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Anode: 10 cm<sup>2</sup> Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(n); cathode: 10 cm<sup>2</sup> stainless steel foil. *Insets* UV-vis absorption spectra collected at different times for assays run with the Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) anode at 10 mA cm<sup>-2</sup>

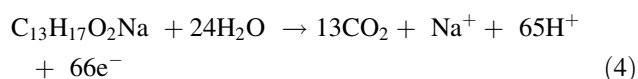


**Fig. 6** Relative COD decay for the assays run with the different pollutants (**a** AM; **b** CA; **c** DIC; **d** IBU) run at two different current densities, 10 and 30 mA cm<sup>-2</sup>. Experimental conditions: 100 mg L<sup>-1</sup>

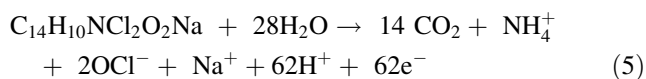
pollutant in 200 mL of 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Anode: 10 cm<sup>2</sup> Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(n); cathode: 10 cm<sup>2</sup> stainless steel foil

complete combustion of the organic pollutant molecule (Eqs. 4, 5), and  $x$  is the number of carbon atoms in the organic compound.

Ibuprofen combustion:



Diclofenac combustion (assuming that Cl is oxidized to OCl<sup>-</sup>):



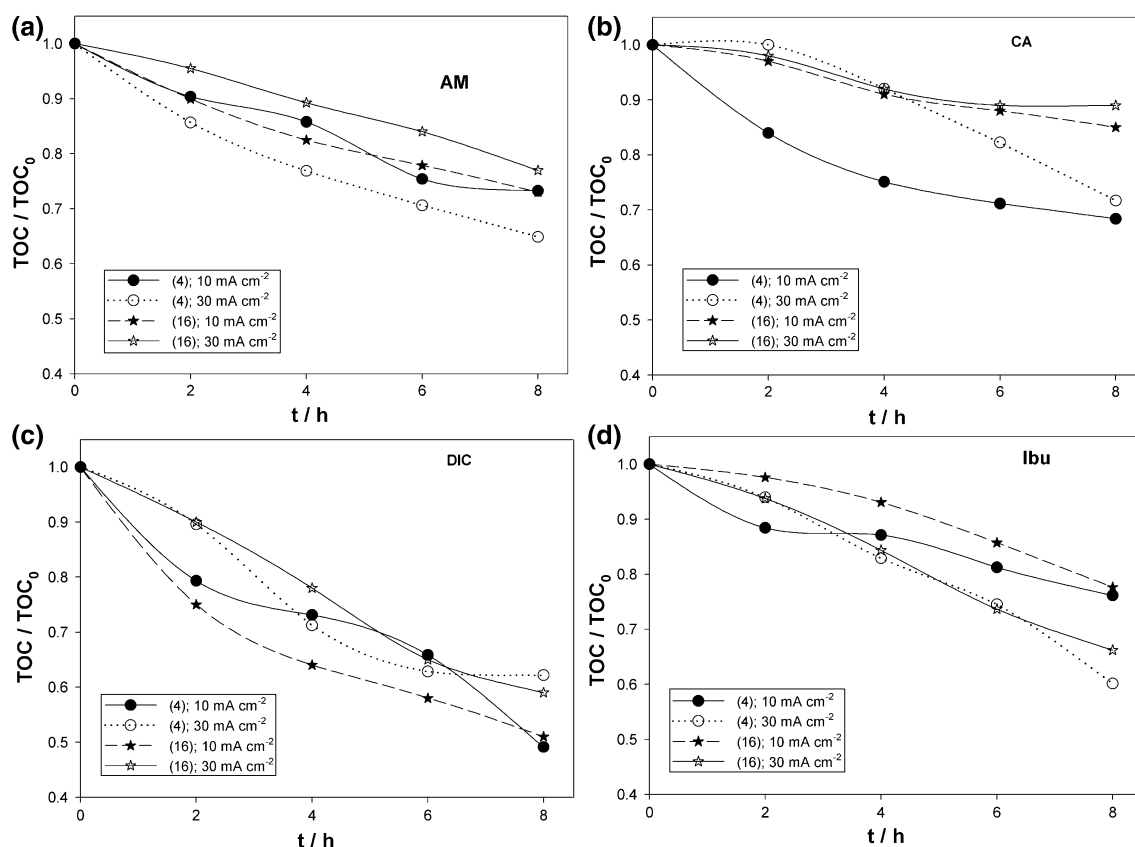
The results obtained for the combustion efficiency are presented in Table 2;  $\eta_c$  increases with the number of Sn/Sb depositions, which is attributed to the increase in the surface roughness and the better coverage of the platinum interlayer, given that platinum is known for promoting conversion rather than combustion. However, despite the absence of platinum and the higher roughness factor presented by the Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> electrode [14], the best combustion efficiencies were obtained with the platinized electrodes prepared in this study.

## 4 Conclusions

The Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> electrodes, prepared by alternating Sn and Sb electrodepositions using 4 or 16 repetitions on a platinized titanium foil, followed by heating in air at 550 °C to form the respective oxides, were proven to be effective in the degradation of amoxicillin, clofibric acid, diclofenac, and ibuprofen. This preparation method is very simple and rapid, especially using Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4). The platinization greatly improved the service life of both materials (Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) and Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16)) when compared to Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> prepared without platinization. In fact, both materials prepared in this work remained functional even after over 500 h of operation. However, when comparison is possible (i.e., assays run with DC and IBU at 10 mA cm<sup>-2</sup>), the results obtained with Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> were slightly better.

The removal of COD increased with current density. Except for diclofenac, the best results in COD removal rate were obtained with the Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(4) electrode. The combustion efficiencies determined for diclofenac and ibuprofen were higher than those obtained with a similar





**Fig. 7** Relative TOC decay for the assays run with the different pollutants (**a** AM; **b** CA; **c** DIC; **d** IBU) run at two different current densities, 10 and 30 mA cm<sup>-2</sup>. Experimental conditions: 100 mg L<sup>-1</sup>

pollutant in 200 mL of 0.035 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. Anode: 10 cm<sup>2</sup> Ti/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(*n*); cathode: 10 cm<sup>2</sup> stainless steel foil

**Table 2** Experimental slopes of the linear fittings of TOC versus COD and combustion efficiencies,  $\eta_C$ , calculated by Eq. 3, for the degradation of the different organic compounds at an applied current density of 10 mA cm<sup>-2</sup>

Compound	Electrode material	<i>n</i>	x	Slope TOC versus CQO	$\eta_C$
Ibuprofen	Ti/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> <sup>a</sup>	66	13	0.133	0.45
	Ti/Pt/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> (4)			0.137	0.46
	Ti/Pt/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> (16)			0.284	0.96
Diclofenac	Ti/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> <sup>a</sup>	62	14	0.267	0.79
	Ti/Pt/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> (4)			0.289	0.85
	Ti/Pt/SnO <sub>2</sub> -Sb <sub>2</sub> O <sub>4</sub> (16)			0.297	0.88

<sup>a</sup> Values obtained from Ref. [14]

electrode material without platinization, especially in the assays run with Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub>(16), which exhibited the highest combustion efficiencies.

The Ti/Pt/SnO<sub>2</sub>-Sb<sub>2</sub>O<sub>4</sub> (4) or (16) electrodes have proved to be electrochemical and mechanically stable. However, the introduction of a Pt layer increased their costs. Thus, to reduce the preparation costs, Pt must be substituted by a cheaper metal that also avoids the formation of an insulating TiO<sub>2</sub> interlayer.

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## References

- Boxall A, Kolpin D, Holling-Sorensen B, Tolls J (2003) Environ Sci Technol 37:287A
- Martinez JL (2009) Environ Pollut 157:2893
- Chopra I, Roberts M (2001) Microbiol Mol Biol Rev 65:232
- Hirsch R, Ternes T, Haberer K, Kratz KL (1999) Sci Total Environ 225:109
- Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT (2002) Environ Sci Technol 36:1202
- Kümmerer K (2009) J Environ Manag 90:2354
- Kötz R, Stuki S, Carcer B (1991) J Appl Electrochem 21:14
- Comminellis Ch, Nerini A (1995) J Appl Electrochem 25:23
- Polcaro AM, Palmas S, Renoldi F, Mascia M (1999) J Appl Electrochem 29:147

10. Sirés I, Cabot PL, Centellas F, Garrido JA, Rodríguez RM, Arias C, Brillas E (2006) *Electrochim Acta* 52:75
11. Ciriaco L, Anjo C, Correia J, Pacheco MJ, Lopes A (2009) *Electrochim Acta* 54:1464
12. Matyasovszky N, Tian M, Chen A (2009) *J Phys Chem A* 113:9348
13. Yang X, Zou R, Huo F, Cai D, Xiao D (2009) *J Hazard Mater* 164:367
14. Ciriaco L, Santos D, Pacheco MJ, Lopes A (2011) *J Appl Electrochem* 41:577
15. Han W, Chen Y, Wang L, Sun X, Li J (2011) *Desalination* 276:82
16. Brinzila CI, Pacheco MJ, Ciriaco L, Ciobanu R-C, Lopes A (2012) *Chem Eng J* 209:54
17. Sirés I, Brillas E (2012) *Environ Int* 40:212
18. Hoflung GB, Cox DF (1981) *Thin Solid Films* 83:261
19. Montilla F, Morallón E, De Battisti A, Vázquez JL (2004) *J Phys Chem* 108:5036
20. Montilla F, Morallón E, Vázquez JL (2005) *J Electrochem Soc* 152:B421
21. Río AI, Molina J, Bonastre J, Cases F (2009) *J Hazard Mater* 172:187
22. Andrade LS, Rocha-Filho RC, Bocchi N, Biaggio SR (2004) *Quim Nova* 27:866
23. Correa-Lozano B, Comninellis Ch, De Battisti A (1997) *J Appl Electrochem* 27:970
24. Chen G, Chen X, Yue PL (2002) *J Phys Chem B* 106:4364
25. Zanta CLPS, Michaud PA, Comninellis Ch, Andrade AR, Boodts JF (2003) *J Appl Electrochem* 33:1211
26. Adams B, Tian M, Chen A (2009) *Electrochim Acta* 54:1491
27. Zhu K, Zhang W, Wang H, Xiao Z (2008) *Clean* 36:97
28. Wang Y, Fan C, Hua B, Liang Z, Sun Y (2009) *Trans Nonferrous Met Soc China* 19:778
29. Yao P, Chen X, Wu H, Wang D (2008) *Surf Coat Technol* 202:3850
30. Chen X, Chen G, Yue PL (2001) *J Phys Chem* 105:4623
31. Andrade LS, Rutuolo LAM, Rocha-Filho RC, Bocchi N, Biaggio S, Iniesta J, García-García V, Montiel V (2007) *Chemosphere* 66:2035
32. Eaton A, Clesceri L, Greenberg A (2005) *Standard methods for examination of water and wastewater*, 21st edn. American Public Health Association, Washington, DC
33. Levine S, Smith AL (1971) *Faraday Discuss Chem Soc* 52:290
34. Wu M, Zhang L, Wang D, Xiao C, Zhang S (2008) *J Power Sources* 175:674
35. Pacheco MJ, Morão A, Lopes A, Ciriaco L, Gonçalves I (2007) *Electrochim Acta* 53:629